Heterogeneous Chemical Processes on the Urban Canopy

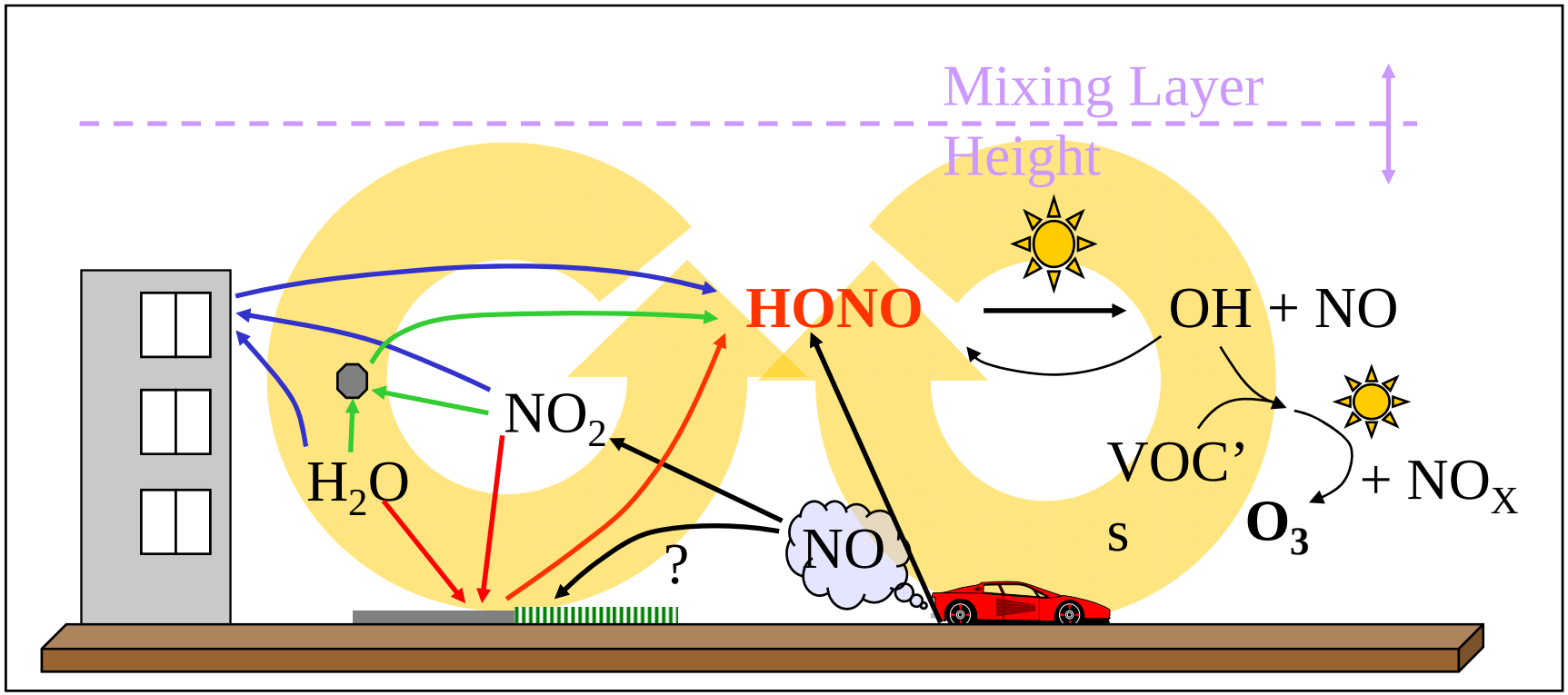
Jochen Stutz, UCLA

Daewon Byun, UH

Motivation

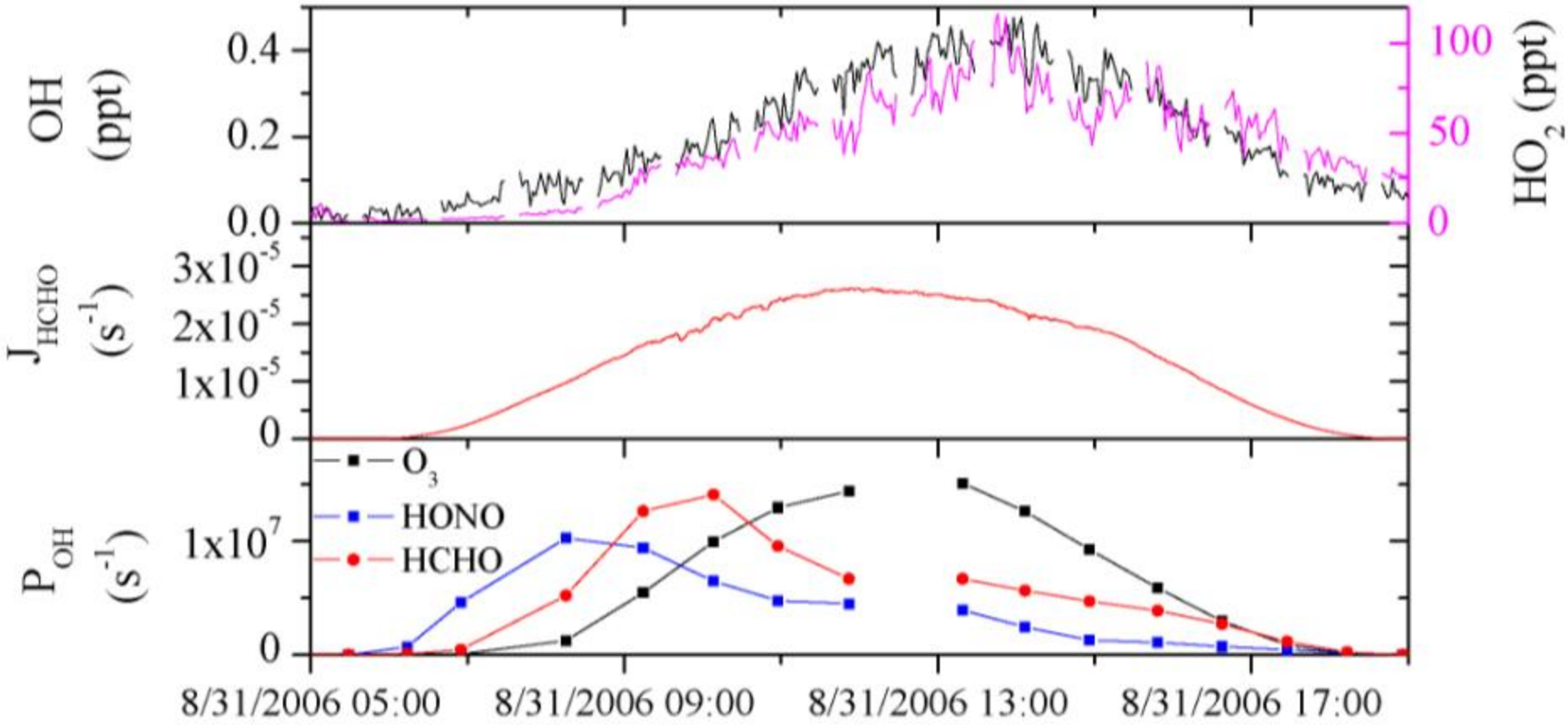
The urban canopy provides a large surface area for chemical processing of urban trace gases. Examples:

- Ozone and NO_2 deposition
- Uptake of NO_3 and N_2O_5
- Conversion of NO_2 to HONO

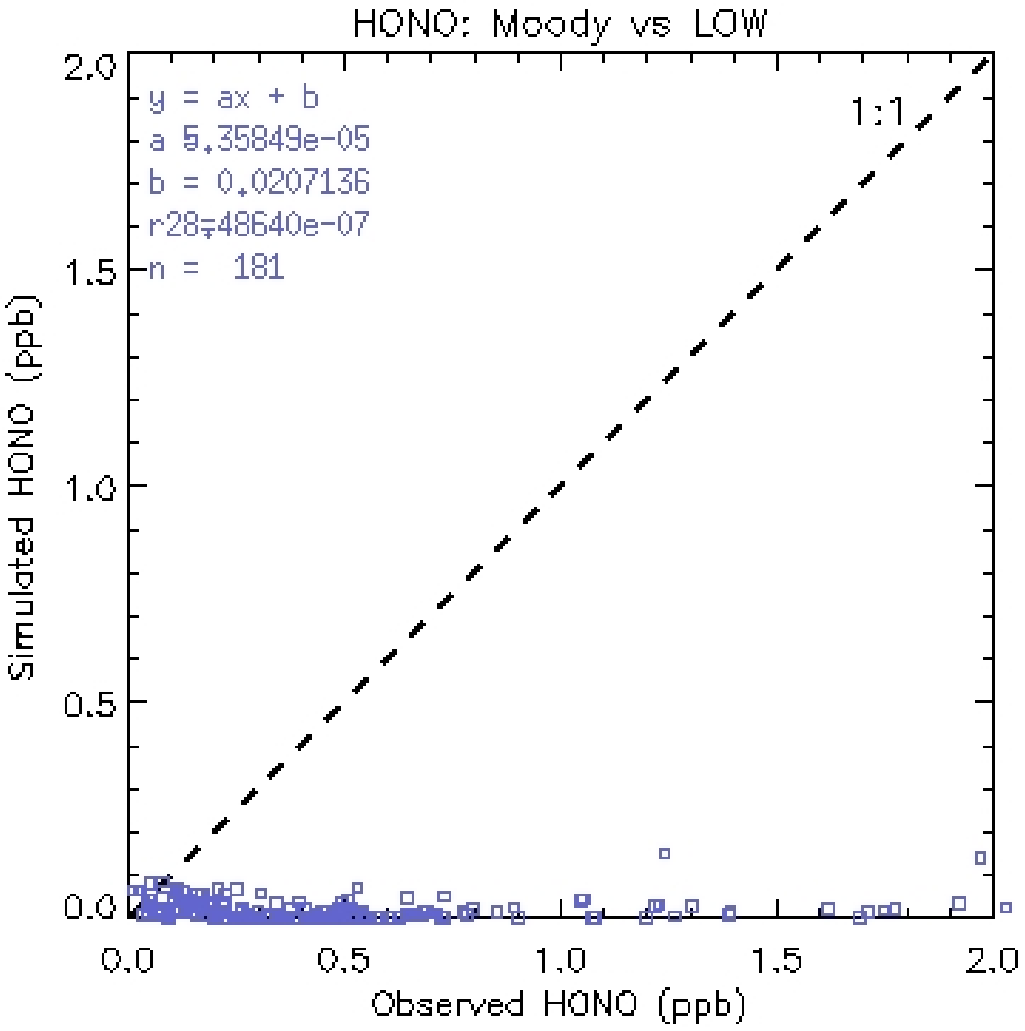


Why is HONO important?

Understanding HONO sources/formation is important for an accurate description of the radical budget in Houston



Comparison of HONO observations and CMAQ-CB4 simulation



Comparison for data from 9/7-9/15/06 for lower LP-DOAS light path (20 – 70m height)

Open Questions on heterogeneous processes, i.e. HONO

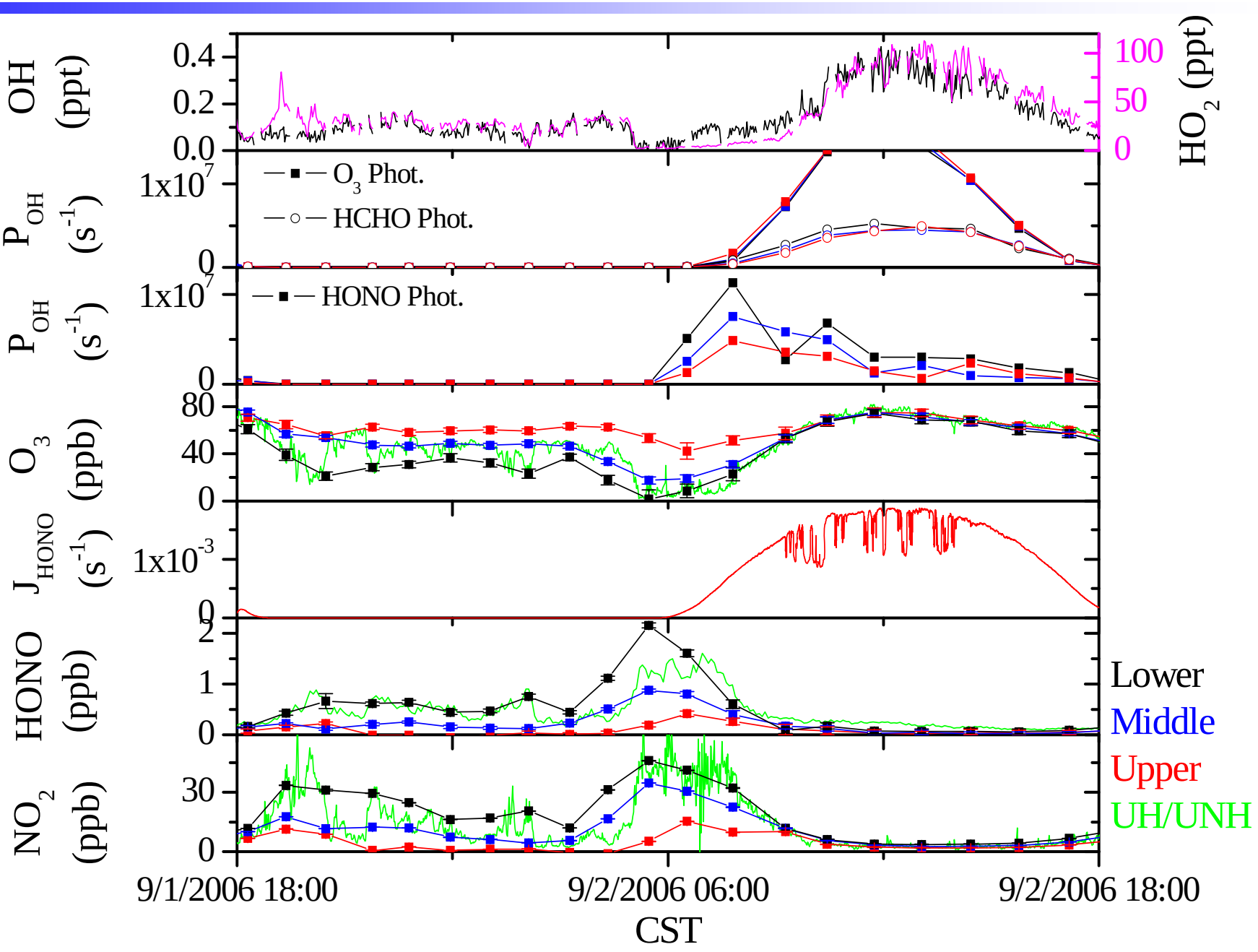
- How is chemistry influenced by vertical transport from the canopy? How well is vertical transport implemented in models, in particular at night?

- What is the surface area of the urban canopy in Houston?

- What is a good parameterization of NO_2 to HONO conversion in models?

- How can we improve the representation of HONO (and N_2O_5) in 3D models of the Houston atmosphere?

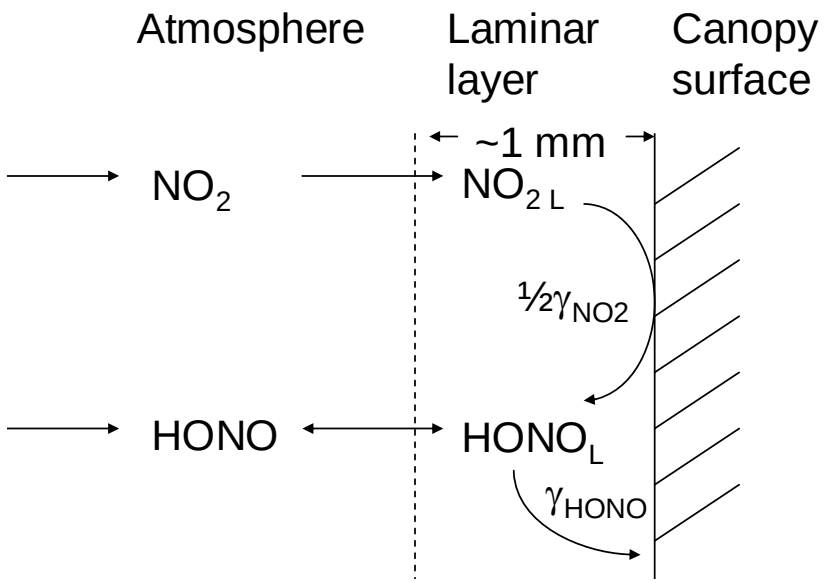
Proposed Work: Analysis of HONO gradients during TRAMP

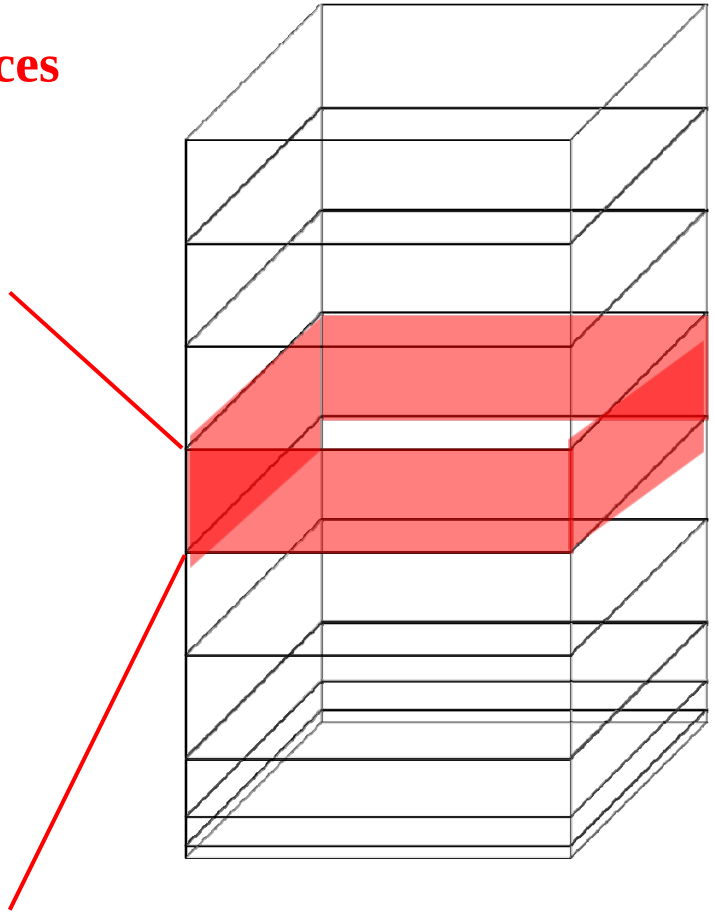


Proposed Work: 1D modeling of Houston boundary layer

- One-dimensional chemical transport model with log/linear spaced layers
- RACM chemical mechanism and emissions of VOC and NO near the ground
- Vertical mixing of scalars and reactive species
- Heterogeneous chemistry at ground and aerosol
- **Explicit treatment of chemistry on building surfaces**
- **HONO chemistry from laboratory experiments on atmospheric surfaces [Trick, 2004]**

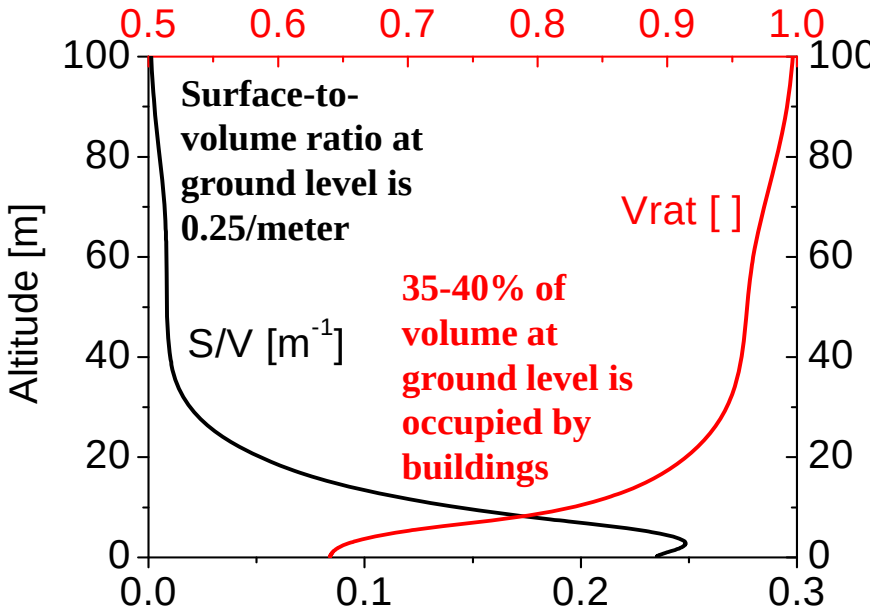
$\gamma_{NO2} = 10^{-5}$
$\gamma_{HONO} = 10^{-4}$



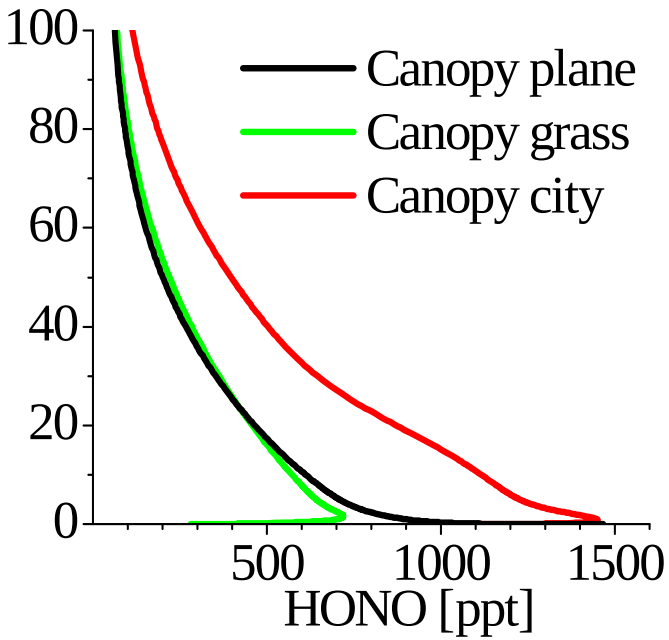


Proposed Work: Influence of urban canopy on chemistry

Example: Santa Monica, CA



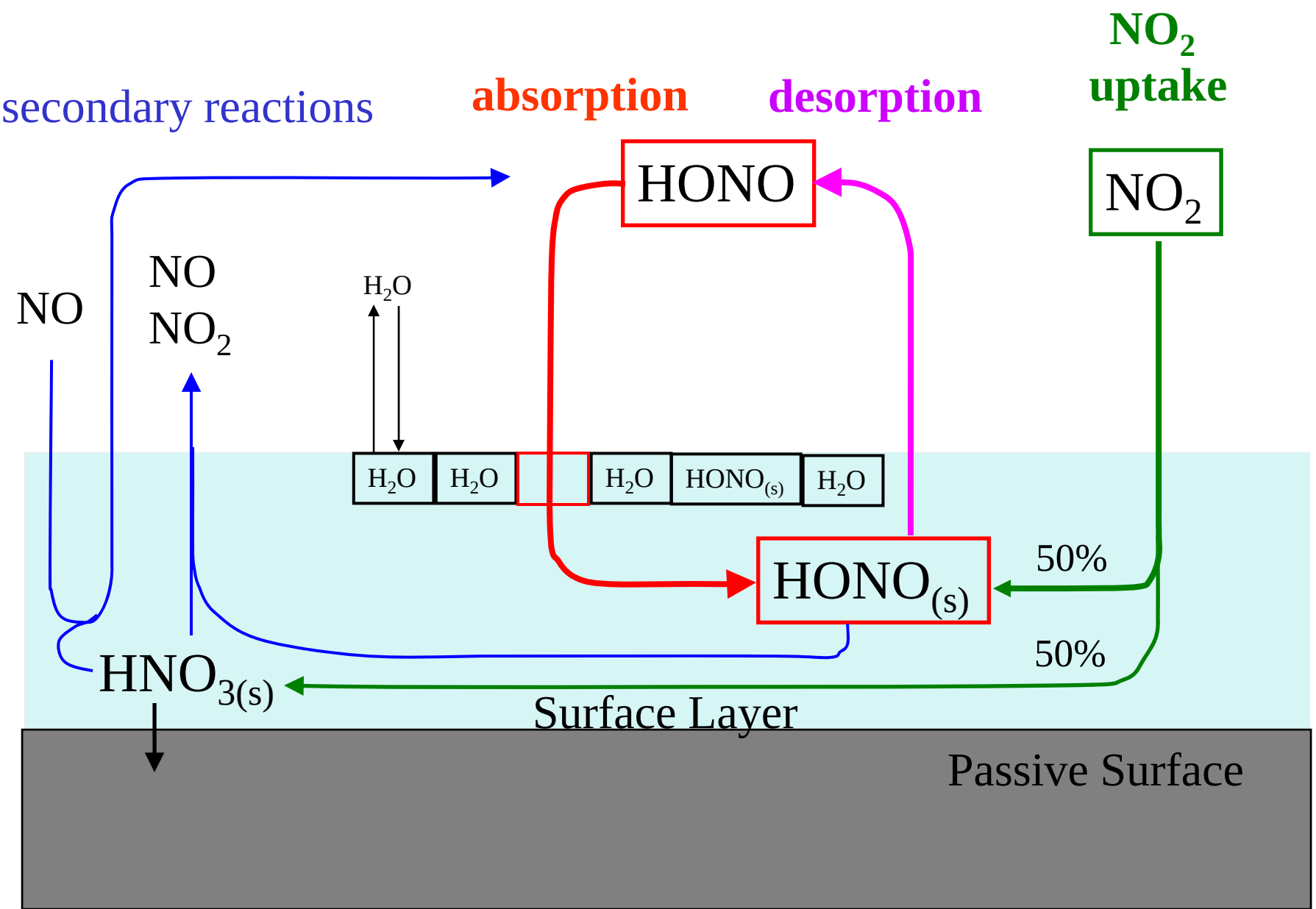
Urban Canopy provides large surface area for heterogeneous chemistry



Impact on HONO in 20m:

Flat Ground:	0.43 ppb
Urban Canopy:	0.86 ppb

Proposed Work: Test HONO formation mechanisms



Conclusions

- Heterogeneous chemistry on the urban canopy and nocturnal vertical mixing are not well described in urban airshed models of Houston. This leads to:
  - inaccurate quantification of the nocturnal NO_x budget
  - uncertainties in the HONO and OH radical levels
- Observations during TRAMP offer unique possibilities to study heterogeneous chemistry.
- A 1D chemical transport model will give insight into heterogeneous processes (HONO formation) on the Houston urban canopy.
- 1D model results can be used to provide better parameterizations for 3D urban airshed models.

Benefits / Deliverables

- Improve predictions of the Houston radical budget and ozone mixing ratios by:
  - Better modeling of heterogeneous chemistry and nocturnal vertical mixing,
  - Better description of OH formation through HONO photolysis.